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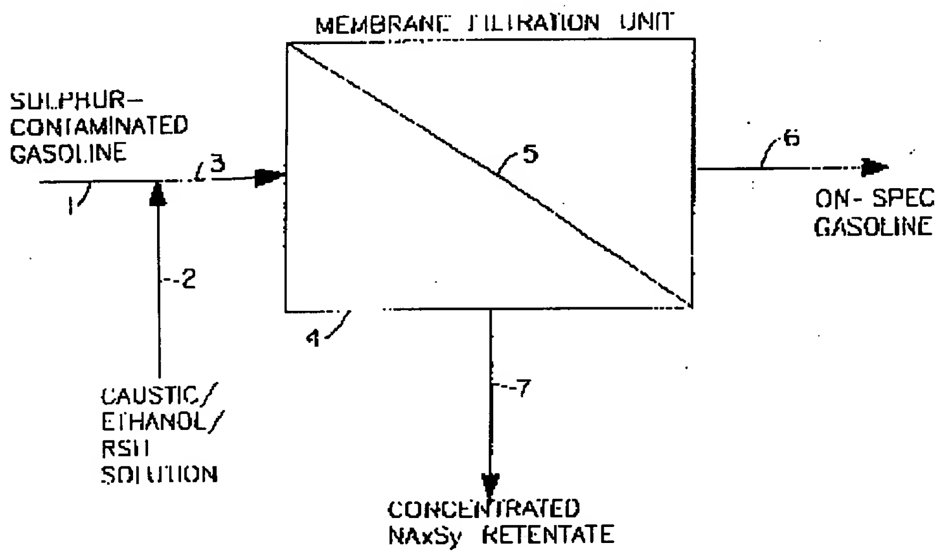
(12) **Patent Application:** (11) **CA 2111176**

(54) MEMBRANE PROCESS TO REMOVE ELEMENTAL SULFUR FROM GASOLINE

(54) PROCEDE A MEMBRANE UTILISE POUR EXTRAIRE LE SOUFRE ELEMENTAIRE DE L'ESSENCE

Representative Drawing:



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ABSTRACT:

ABSTRACT OF THE DISCLOSURE
The present invention relates to a process for removing elemental sulfur from hydrocarbon fluids such as gasoline, liquified petroleum gas, solvents, octane improvers etc. by the steps of combining the hydrocarbon fluid with an inorganic caustic material, an alcohol, and an organo - mercaptan compound capable of reacting with sulfur to form an insoluble polysulfide reaction product at ambient reaction temperature, passing the hydrocarbon fluid containing the insoluble polysulfide precipitate to a membrane separation unit wherein the hydrocarbon fluid is contacted with a microfiltration or ultrafiltration membrane under an applied pressure, thereby producing a permeate stream comprising hydrocarbon fluid of reduced sulfur content

and a retentate stream comprising the polysulfide of reduced hydrocarbon content.

CLAIMS: Show all claims

*** Note: Data on abstracts and claims is shown in the official language in which it was submitted.

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(19) (CA) APPLICATION FOR CANADIAN PATENT (12)

(54) Membrane Process to Remove Elemental Sulfur from Gasoline

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Notice: This application is as filed and may therefore contain an incomplete specification.

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Background of the Invention

Field of the Invention

This invention is directed to a process for removing the elemental sulfur content of hydrocarbon fluids by the steps of contacting the hydrocarbon fluid with an inorganic caustic, an alcohol and a mercaptan or sulfide to convert the sulfur into insoluble polysulfides, passing the hydrocarbon fluid containing the insoluble polysulfide to a membrane separation unit wherein the hydrocarbon fluid is contacted with one face of a selective membrane under pressure wherein the pressure used is such that the pressure/membrane pore size relationship falls within the operable region of Figure 2 to thereby produce a permeate comprising the hydrocarbon fluid of reduced sulfur content and a retentate containing the insoluble polysulfide.

Description of the Related Art

The presence of sulfur and sulfur compounds in hydrocarbon fluids such as gasoline, solvents, liquified petroleum gases, octane improvers, etc. is highly undesirable. Sulfur in such fluids is corrosive to equipment using or storing such fluids. It also renders such fluids off spec and can make them unusable for their intended purpose.

The sulfur can be acquired in any number of ways such as through contamination in storage, contamination during shipping such as through pipe lines or tank cars or trucks.

Because of this it has not proven feasible to transport certain hydrocarbon fluids such as gasoline for which there are very stringent sulfur control specifications, through pipelines used to transport other fluids, such as crude or refined oils. The presence of residual amounts of such fluids in the pipeline even following purging or pegging is sufficient to contaminate subsequent streams such as gasoline with sufficient sulfur to render such gasoline off spec and unmerchantable.

Various techniques have been reported for removing elemental sulfur from petroleum products. For example U.S. Patent 4,149,966 discloses a method for removing elemental sulfur from refined hydrocarbon fuels by adding an organo-mercaptan compound and a copper compound capable of forming a soluble complex with said mercaptan and said sulfur and contacting said fuel with an adsorbent material to remove the resulting copper complex and substantially all the elemental sulfur.

U.S. Patent 4,908,122 discloses a process for sweetening a sour hydrocarbon fraction containing mercaptans by contacting the hydrocarbon fraction in the presence of an oxidizing agent with a catalytic composite, ammonium hydroxide and a quaternary ammonium salt other than hydroxide.

U.S. Patent 3,185,641 describes a method for removing elemental sulfur from a liquid hydrocarbon which comprises contacting with solid sodium hydroxide a hydrocarbon stream having dissolved therein at least 7.6 parts by weight of water per part of sulfur contained therein to yield both a hydrocarbon phase and an aqueous phase. The method is claimed to be effective and convenient for treating gasoline containing from trace to more than 25 ppm sulfur employing temperatures as high as about 140°F (60°C).

U.S. Patent 4,011,882 discloses a method for reducing sulfur contamination of refined hydrocarbon fluids transported in a pipeline for the transportation of sweet and sour hydrocarbon fluids by washing the pipeline with a wash solution containing a mixture of light and heavy amines, a corrosion inhibitor, a surfactant and an alkanol containing from 1 to 6 carbon atoms.

U.S. Patent 3,556,990 discloses the purification of hydrocarbon fuels by forcing the fuel under pressure through a hydrocarbon - insoluble crosslinked oleophylic membrane. The process removes sulfur compounds, bacteria and other non-hydrocarbon contaminants by utilizing reverse osmosis at 50 to 300 atmospheres. The contaminant laden retentate can be purified by chemical processing or by reverse

osmosis then recycled to the primary reverse osmosis membrane for further purification. It is reported that one contaminant which passes through the membrane is long chain mercaptans which are removed by alkaline washing.

The Present Invention

The present invention provides a process for removing elemental sulfur from hydrocarbon fluids such as hydrocarbon fuels, fuel blending components such as octane improvers, liquified petroleum gas (LPG), solvents and other petroleum streams transported in a pipeline for the transportation of sour hydrocarbon streams, comprising contacting the sulfur-containing fluid with an inorganic caustic material, an alcohol and an organo mercaptan compound capable of reacting with sulfur to form an insoluble polysulfide reaction product at ambient reaction temperatures. The treated fluid is then contacted under an applied pressure with one face of a selective membrane whereby a hydrocarbon rich-insoluble polysulfide lean permeate is produced while conversely an insoluble polysulfide rich-hydrocarbon lean retentate is also produced, as compared to the hydrocarbon fluid-insoluble polysulfide contents of the original feed.

Brief Description of the Figures

Figure 1 is a simplified schematic of the process of the present invention.

Figure 2 presents the relationship between membrane pore size and applied feed pressure which must be observed to achieve operability and selectivity.

Figure 3 is a schematic of a preferred embodiment of the present process including retentate recycle to increase hydrocarbon recovery.

Detailed Description of the Invention

In the present invention, sulfur present in hydrocarbon fluids is converted into insoluble polysulfides by adding an inorganic caustic, an alcohol and an organo-mercaptan or sulfide and the precipitated insoluble polysulfide is removed by ultrafiltration under particular conditions of pressure in relation to membrane pore size. The use of inorganic caustic, alcohol and organo-mercaptan or a sulfide to convert the sulfur in hydrocarbon fluids into insoluble polysulfides is taught in copending application USSN 715,959 filed June 17, 1991 in the names of Poirier, Falkiner, Kraemer, Gilbert and Campbell, the disclosure of which is incorporated herein by reference.

Useful organo-mercaptans include a wide variety of compounds having the general formula RSH, where R represents an organic radical which may be alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl or arylalkyl having from 1 to about 16 carbon atoms. Thus, the radical may be, for example, methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl, t-butyl, amyl, n-octyl, decyl, dodecyl, octadecyl, phenyl, benzyl and the like. Most preferably, RSH is an alkyl mercaptan containing 2 to 5 carbon atoms.

In another embodiment the mercaptan may be combined with or replaced by a sulfide such as K_2S, Na_2S, NaHS, Li_2S, H_2S and the like.

The inorganic caustic material which is employed includes alkali metal or ammonium hydroxides having the formula MOH wherein M is selected from the group consisting of lithium, sodium, potassium, NH_4, or mixtures thereof. M is most preferably sodium or potassium. As a result of the use of the inorganic caustic material, the resultant sulfur products are insoluble in the treated fluids and may be removed by the use of adsorbents and/or filtration.

Alcohols are employed as a phase transfer or solubilizing agent. Accordingly, a number of alcohols may be used for this purpose. Alcohols which may be used include, among others, C_1 to C_{10}

monoalcohols, more preferably C_1 to C_4 monoalcohols in which the other reagents are soluble. Other alcohols, polyols, glycols, polyglycols, glycol ethers and related materials capable of solvating the caustic for the purpose of effecting the reactions may also be used. Examples of preferred alcohols include methanol, ethanol, n-propanol, i-propanol, n-butanol, i-butanol and t-butanol.

The fluids which are treated in accordance with the invention include fluids containing elemental sulfur where the elemental sulfur is detrimental to the performance of the fluid.. The invention is particularly applicable to those liquid products which have become contaminated with elemental sulfur as a result of being transported in a pipeline previously used to transport sour hydrocarbon streams such as petroleum crudes.

The fluids treated in accordance with the invention include a wide variety of petroleum fuels and particularly refined hydrocarbon fuels such as gasoline, jet fuel, diesel fuel and kerosene.

Other fluids include ethers used to improve the octane ratings of gasoline. These ethers are typically dialkyl ethers having 1 to 7 carbon atoms in each alkyl group. Illustrative ethers are methyl tertiary-butyl ether, methyl tertiary-amyl ether, methyl tertiary-hexyl ether, ethyl tertiary-butyl ether, n-propyl tertiary-butyl ether, isopropyl tertiary-amyl ether. Mixtures of these ethers and hydrocarbons may also be treated in accordance with the invention.

In general, the process involves the addition to the fluid to be treated of effective amounts of one or a mixture of RSH organo mercaptan compounds, the alcohol and the caustic material as defined above to allow for the in-situ formation of an insoluble polysulfide salt. Most preferably, the caustic material is added to the fluid as a solution in the alcohol, and the organo mercaptan is added separately.

The treating conditions which may be used to produce the insoluble polysulfides are conventional. Contacting of the fluid to

be treated is effected at ambient temperature conditions, although higher temperatures up to 100°C or higher may be employed. Substantially atmospheric pressures are suitable, although pressures may, for example, range up to 1000 psig. Contact times may vary widely depending on the fluid to be treated, the amount of elemental sulfur therein and the treating materials used. The contact time will be chosen to effect the desired degree of elemental sulfur removal. In most cases, the reaction proceeds relatively fast, usually within a few minutes. Contact times ranging from 30 seconds to a few hours will usually be adequate.

The reactants may be dispersed within the fluid to be treated using any suitable mixing device which will provide maximum mixing with the fluid. The process is particularly adapted for continuous operation wherein a static mixer is employed and the reactants are injected into a moving flow of the fluid prior to entry into the static mixer. Residence time in the mixer should be sufficient to maximize the formation of fluid insoluble sulfur/mercaptan polysulfide reaction product.

The amount of caustic used in accordance with the invention may range within wide limits, for example, from about 0.1 to 10.0 moles, preferably from about 0.5 to 2.0 moles, of caustic (MOH) per mole of elemental sulfur present in the fluid to be treated.

The amount of organo mercaptan and/or sulfide used in accordance with the invention generally ranges from 0.1 to about 2.0 moles, preferably from about 0.5 to 0.7 moles, of organo mercaptan and/or sulfide per mole of elemental sulfur present in the fluid to be treated.

As mentioned, the alcohol serves as solubilizing agent. The amount of alcohol present may therefore vary within wide limits. Typically, the amount of alcohol will range from about 100 to about 2500 volume parts per million (vppm) of the fluid being treated.

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Fluids containing quantities of elemental sulfur as high as 100 mg, or higher, sulfur per liter, more usually from about 10 to about 60 mg per liter, can be effectively treated in accordance with this invention to reduce the elemental sulfur contamination to about 5 mg sulfur per liter or lower.

The hydrocarbon fluid containing the insoluble polysulfides is then contacted with one face of a membrane, under an applied pressure to effect the separation of the insoluble polysulfide from the hydrocarbon fluid resulting in a hydrocarbon fluid of reduced sulfur content.

It is unexpected that sulfur contaminated hydrocarbon fluid can be purified in this manner using membrane separation because the shape and texture of the precipitated polysulfide species is virtually impossible to determine. Thus, whether the particles are hard or soft, sticky or slippery is not known. As a consequence of these unknowns the size and type of membrane which can be used cannot be predicted.

Another essential feature is that any such process must recover virtually all of the available hydrocarbon fluid involved if it is to be economically viable.

The membrane employed in the present process can be either a microfiltration or ultrafiltration membrane having a pore size in the range 1 to 0.01 µm, preferably 0.5 to 0.01 µm, employed under an applied pressure of from 1 to 1000 psig, preferably 1 to 500 psig, wherein lower applied pressure within the aforesaid ranges are employed when utilizing membranes having the larger pore sizes. This is presented in Figure 2 which shows the relationship between membrane pore size and applied pressure. The region of operability under the curve corresponds to those combinations of pore size and pressure wherein the recovered hydrocarbon fluid is clear and bright, indicating an absence of insoluble polysulfide and wherein the recovered hydrocarbon has minimal residual caustic as determined by phenolphthalein titration.

In the present process, as presented in Figure 1 the hydrocarbon fluid (line 1) is mixed with inorganic caustic/alcohol/organic mercaptan (line 2) and the mixture, after a sufficient time for the formation of insoluble polysulfides, is fed via line 3 to a membrane separation unit 4 wherein the feed mixture is contacted with one face of the membrane (5) under an applied pressure to recover a sulfur free hydrocarbon fluid via line (6) as permeate and a retentate of concentrated insoluble polysulfide via line (7).

The membrane used can be either hydrophobic or hydrophilic in nature and either polymeric, ceramic, sintered glass or sintered metal, etc., so long as the pressure - pore size relationship falls within the disclosed range.

Example

A lab unit was set up which consisted of a 2 liter feed reservoir. To a batch gasoline sample containing 40 mg/L of elemental sulphur was added propyl mercaptan (PrSH) and NaOH (dissolved in ethanol) at a molar ratio to elemental sulphur in the feed of S:NaOH:PrSH = 1:0.7:0.7 with the total ethanol content being 1200 vppm. The resulting hazy gasoline was placed in the 2 L reservoir. A 5 L/min pump was used to circulate the feed across a cell housing the membrane. The permeating material (permeate) was collected in a graduated cylinder. The membrane flux was calculated as follows:

Flux = amt of permeate collected in liters/time in days/membrane area in m^2

The clarity (i.e., clear and bright) was visually assessed while the residual caustic was determined by phenolphthalein titration. A clear color in the phenolphthalein test was considered a pass while a pink color indicated a failure.

Table 1 summarizes the results. Comparing the performance of the 1 micron regenerated cellulose and 0.1 micron teflon membranes indicates that the minimum pore size requirement is less than 1

micron. However, applying 5 to 10 psig feed pressure to the 0.1 micron teflon membrane resulted in a hazy permeate which also failed the phenolphthalein test. This indicates that feed pressure also affects performance. Figure 2, which illustrates the operable region, shows that the membrane pore size must be reduced as the feed pressure is increased.

In order to recover essentially all of the hydrocarbon fluid a multi-stage (preferably 2) membrane separation scheme as shown in Figure 3 would be required.

The hydrocarbon feed in line 1 is combined with caustic/-alcohol/mercaptan from line 2 in the mixing valve 3 and fed via line 3a to a first membrane separation stage (4) wherein the feed is contacted under pressure with one face of a membrane (4a). Most of the feed is recovered from the first membrane separation stage via line 5 as hydrocarbon fluid of reduced sulfur content (e.g., on spec gasoline) while a minor quantity is recovered as retentate via line 6 which contains the bulk of the insoluble polysulfide and a minor quantity of hydrocarbon fluid.

The retentate via line 6 is fed into a vessel 7 and then via line 8 into a second membrane separation unit (9) wherein it is contacted with a selective membrane (10). Purified hydrocarbon fluid is recovered via line 11 and mixed with the purified hydrocarbon fluid from separation unit 4 in line 5.

The retentate is recycled via line 12 to unit 7 for recycle to extinction in separation unit 9. Periodically, accumulated solids and insoluble polysulfides which build up on vessel 7 are removed via flush line 13. This would be achievable where the contaminated gasoline is handled in batches as is the case at many terminals. In areas where a continuous process is required two parallel second stage units can be utilized whereby one unit is on-line while another is being cleaned.

Table 1

Effect of Pore Size and Pressure on Membrane Performance

(25 C, 5 L/min feed flow, Feed: 40 mg/L elemental S in untreated gasoline)

Membrane	Pressure (psig)	Flux (kL/m2-d)	Clarity(1)	Phenolphth
1 um - Regenerated Cellulose	2	>80	hazy	fail
0.1 um - Teflon	2	13-80	C&B	pass
	5-10	>80	hazy	fail
0.04 um - Nylon	7	14	C&B	pass
	100	40	C&B	pass
0.04 um Polypropylene	50	4.5	C&B	pass
	100	9	C&B	pass
0.01 um Polyimide	50	2.5	C&B	pass
	100	3.7	C&B	pass

(1) - C&B solutions contain <3 mg/L elemental sulphur

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A process for removing elemental sulfur from hydrocarbon fluids by the steps of combining the hydrocarbon fluid with an inorganic caustic material, an alcohol, and an organo-mercaptan compound or a sulfide capable of reacting with sulfur in the hydrocarbon fluid to form an insoluble polysulfide reaction product, passing the hydrocarbon fluid containing the insoluble polysulfide precipitate to a membrane separation unit wherein it is contacted with a microfiltration or ultrafiltration membrane under an applied pressure, said applied pressure being a pressure selected such that with respect to the pore size of the membrane the pressure/pore size relationship falls within the operable region of Figure 2, thereby producing a permeate comprising the hydrocarbon fluid of reduced sulfur content and a retentate containing the insoluble polysulfide.

2. The process of claim 1, wherein the hydrocarbon fluid is gasoline, jet fuel, diesel fuel, kerosene or ether.

3. The process of claim 1, wherein the membrane has a pore size in the range 1 to 0.01µm and the pressure used is in the range of from 1 to 1000 psig.

4. The process of claim 3 wherein the membrane is teflon, nylon, polypropylene or polyimide.

ABSTRACT OF THE DISCLOSURE

The present invention relates to a process for removing elemental sulfur from hydrocarbon fluids such as gasoline, liquified petroleum gas, solvents, octane improvers etc. by the steps of combining the hydrocarbon fluid with an inorganic caustic material, an alcohol, and an organo - mercaptan compound capable of reacting with sulfur to form an insoluble polysulfide reaction product at ambient reaction temperature, passing the hydrocarbon fluid containing the insoluble polysulfide precipitate to a membrane separation unit wherein the hydrocarbon fluid is contacted with a microfiltration or ultrafiltration membrane under an applied pressure, thereby producing a permeate stream comprising hydrocarbon fluid of reduced sulfur content and a retentate stream comprising the polysulfide of reduced hydrocarbon content.

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FIG. 1

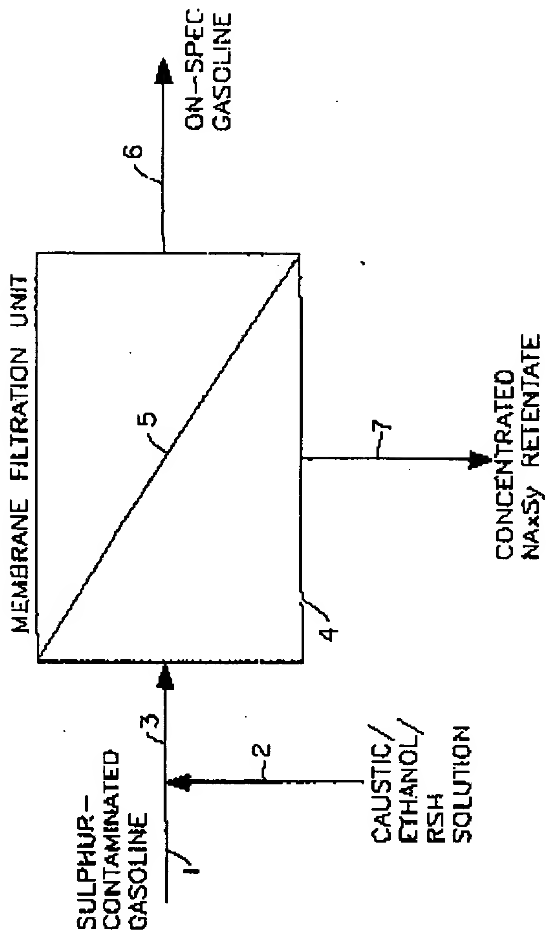

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FIG. 2

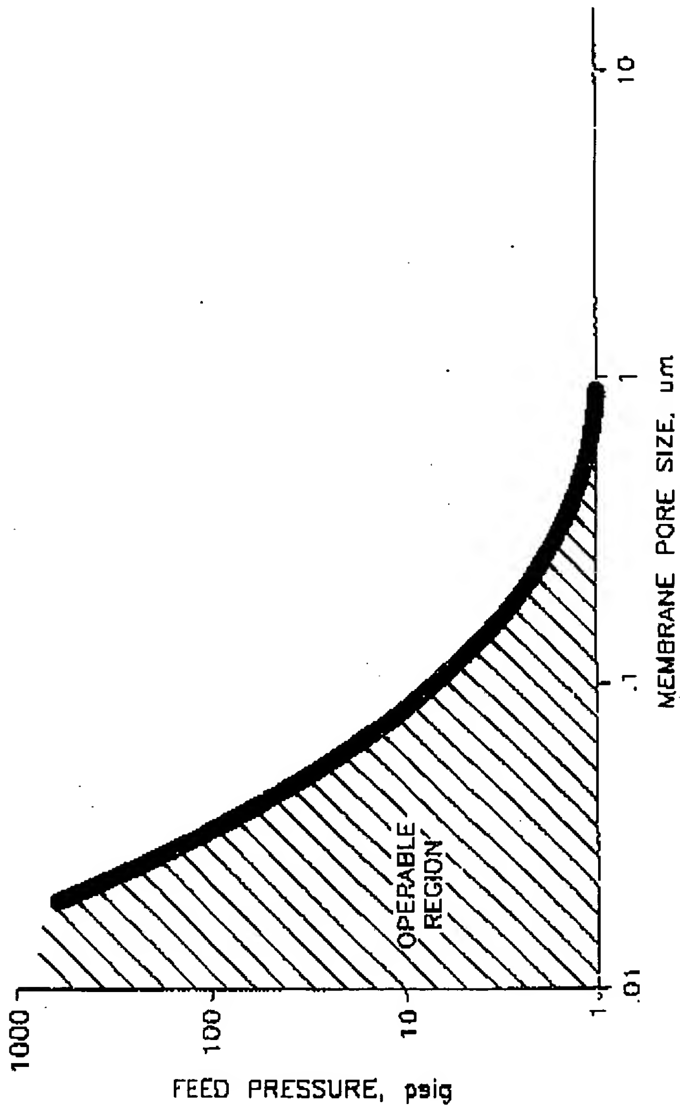

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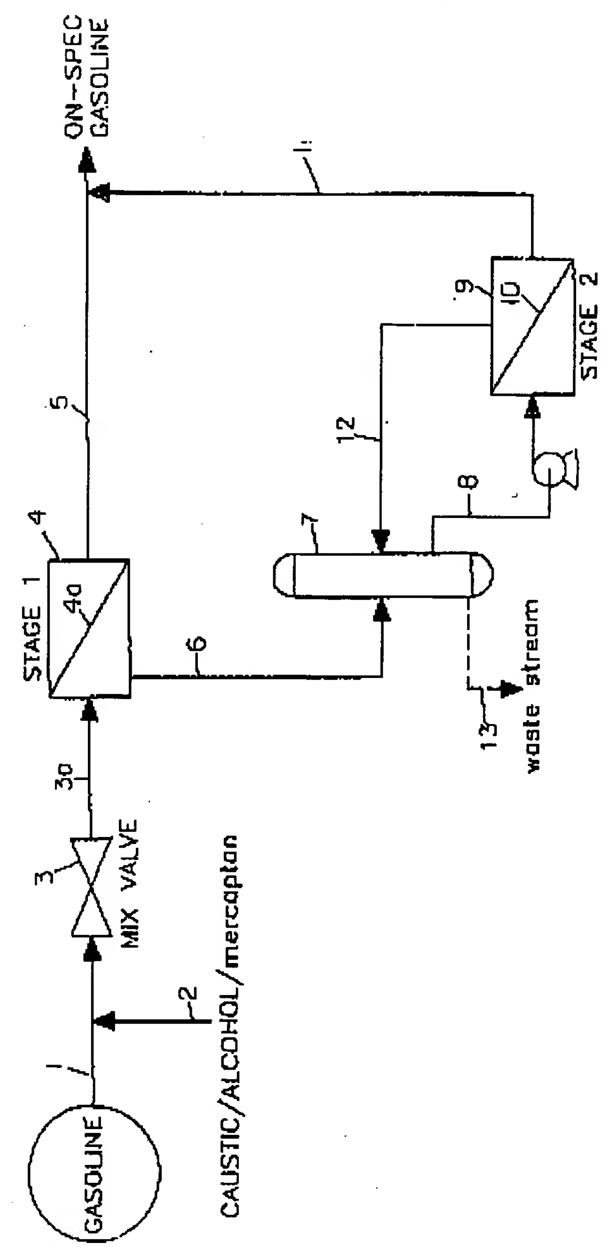
FIG. 3



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